Solid Sorbents as a Solid Retrofit CO$_2$ Capture Technology: Results from Field Testing

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ABSTRACT

ADA Environmental Solutions, through a DOE Cooperative Agreement and support from EPRI and several power industry partners, is evaluating the potential of post combustion CO$_2$ capture using solid sorbents. Many solids have lower heat capacity and higher CO$_2$ working capacity than leading solvents. Thus, solids-based systems have the potential to drastically reduce projected capture costs due to lower regeneration energy required to release the purified CO$_2$. The results and lessons learned during 1 kW pilot evaluations conducted on a slipstream of flue gas from a coal-fired power plant are discussed.

INTRODUCTION

There is significant public pressure to reduce emissions of greenhouse gases. International scientists have identified CO_2 produced by the burning of fossil fuels is a significant contributor to the increase in baseline CO_2 concentrations and ongoing discussions are occurring at the state and federal levels regarding future regulation of CO_2 emissions. Stationary point sources, such as coal-fired power plants, offer one of the most feasible options for significant emission reductions in the foreseeable future. Currently, half of the electricity in the United States is generated using coal, amounting to 320 GW.[1] New generation can be designed for carbon capture and increased efficiency, but the carbon emissions from the conventional coal-fired power plants must be addressed. Post-combustion capture technologies are being developed rapidly in order to meet the carbon management needs of the existing fleet of power plants. These technologies are widely varied in the mechanism of separation and it is expected that a portfolio of carbon capture options will be necessary to address the wide array of coal types, air pollution control systems, and operating conditions.

Solid sorbents are one of the many promising CO_2 capture technologies in the early stages of development. Although CO_2 capture by solid sorbents has yet to be demonstrated on the scale necessary to prove commercial viability for coal-fired power generation units, this is not a new technology. For years, solid sorbents designed for CO_2 capture have been used to purify breathing air in confined spaces such as space shuttles and submarines.[2] Potential advantages of solid sorbents over other CO_2 capture options, such as aqueous amines, are as follows:

- Safe material for local environment and low disposal/treatment costs
- Higher CO_2 capacity
- Lower regeneration energy
- Multi-pollutant control

Potential technical hurdles for the use of solid sorbents in a temperature swing system for CO_2 capture are as follows:

- Feedstock supply
- Movement of material and related attrition
- Temperature control and heat transfer management

Sorbents can be classified into two general families: those that chemically react with the CO_2, called supported reactants, and those that adsorb or use their molecular structure to screen CO_2 from other gases, called non-reacting adsorbents. For both types of sorbents, the act of separating CO_2 from the flue gas will be exothermic; recovering the CO_2 from the sorbent is endothermic and will require heat input. Budgeting the thermal energy is a top priority when developing an economically feasible full-scale process. Although coal-fired power plants are experienced with solids handling, the design of the contactor (adsorption and regeneration) must still be developed and optimized for this application.

Chemical sorbents that react with the CO_2 in the flue gas include a support, which usually has a high surface area, with an immobilized amine or other reactant on the surface. The surface area provides for numerous sites for the desired reaction to occur. Examples of commonly used

supports are alumina or silica, while common reactants include amines such as polyethylenimine[3,4] or other chemicals which react with CO_2 to form carbamates and bicarbonates. When heated, the reaction will reverse, releasing the CO_2, and often water, which can then be separated from each other during cooling and compression. After this step, the pure CO_2 can be geologically sequestered.

Physical adsorbents can separate the CO_2 from the other flue gas constituents, but do not react with it. Instead, they use their cage-like structure to act as molecular sieves or adsorb it onto their surface. These sorbents can be regenerated using a pressure swing and/or a temperature swing, although the costs associated with pressure swing may be prohibitively high. Physisorbents such as activated carbon and zeolites are non-toxic, and could be relatively inexpensive to manufacture.

DOE laboratories and independent universities have spearheaded many solid-sorbent development projects geared towards CO_2 capture. This research encompasses a wide range of technical areas, including carbonate chemical sorbents, metal organic frameworks (MOFs), amine grafted zeolites, and supported amine sorbents.[5,6] Key sorbent performance characteristics include:

1. Working CO_2 capacity (when reported as a percentage): $\dfrac{100 * mass_{CO_2-removedfromgas}}{mass_{sorbent}}$

2. Regeneration potential (i.e. cyclic stability): ability of a sorbent to be used repeatedly without any reduction in capacity

3. Poisoning from other flue gas constituents: Decrease in capacity due to SO_2, NO_x, etc.

4. $\Delta T_{capture-regen}$: The difference between capture and regeneration temperatures

Although solid sorbents are a promising CO_2 capture technology, the majority of development and evaluation is currently being conducted on the laboratory-scale using compressed gases. To advance this technology to the next level, it is important to test sorbents on actual flue gas at scales large enough to identify potential operational issues.

The US Department of Energy (DOE), through the National Energy Technology Laboratory's (NETL) Existing Plants, Emissions and Capture (EPEC) program is funding projects to develop technologies capable of achieving at least 90% CO_2 capture from coal-fired electric generating units that do not increase the cost of producing electricity by more than 35%.

Through a cooperative agreement from DOE/NETL with industry cost share, ADA has been managing a program to evaluate the viability of solid sorbents for post-combustion CO_2 capture at coal-fired power plants. ADA and Southern Company have collaborated to design, fabricate, and operate a unique 1 kW pilot designed to test different CO_2 sorbents on actual flue gas. The first sorbent, a supported amine, has been evaluated at the 1 kW scale with several promising results regarding the potential viability of solid sorbents for achieving the DOE/NETL goals and for providing guidance on sorbent and process development needs.

EXPERIMENTAL METHODS

Sorbent Selection

The 1 kW pilot was designed and fabricated to evaluate CO_2 sorbents on a slipstream of actual flue gas in a fluidized-bed arrangement. Sorbents for 1 kW testing were down-selected from more than 100 screened by ADA-ES at the laboratory scale. Since one of the most important advantages of solid sorbents is the potential to reduce the regeneration energy compared to aqueous systems, the theoretical regeneration energy for each material was calculated and used as a selection criterion for the selection process. The theoretical regeneration energy is a function of the heat input required to increase the temperature of the sorbent (i.e. sensible heat) as well as the energy required to overcome the endothermic reaction to release the CO_2. A summary of the laboratory screening results, showing the theoretical regeneration energy for several materials compared to aqueous MEA (represented by the dashed line)[3], is presented in Figure 1. The specific heat of the materials has not been measured by ADA in several cases, but when a value was not available, it was usually assumed to be in the range of 0.8 to 1.3 kJ/kg K, depending on the raw materials. The results from three different sorbent types are shown in this figure: carbon-based materials (left, black), supported amines (middle, blue), and zeolites (right, yellow).

The sorbent selection criteria for 1 kW testing included
- Theoretical regeneration energy significantly lower than that of aqueous MEA
- Demonstration of cyclic stability in the laboratory test fixture after a minimum of 250 adsorption/regeneration cycles on simulated flue gas
- Projected commercial-scale availability of required raw materials

Several supported amines and activated carbons have been identified as candidates for testing at the 1 kW pilot scale. To date the 1 kW pilot evaluation of sorbent R is complete and results are included in this paper. Sorbent R consists of mesoporous silica coated with an amine. Both the amine and the silica are produced commercially today, although neither is currently produced on the scale necessary to meet the required demand if this sorbent was widely used for post-combustion CO_2 capture.
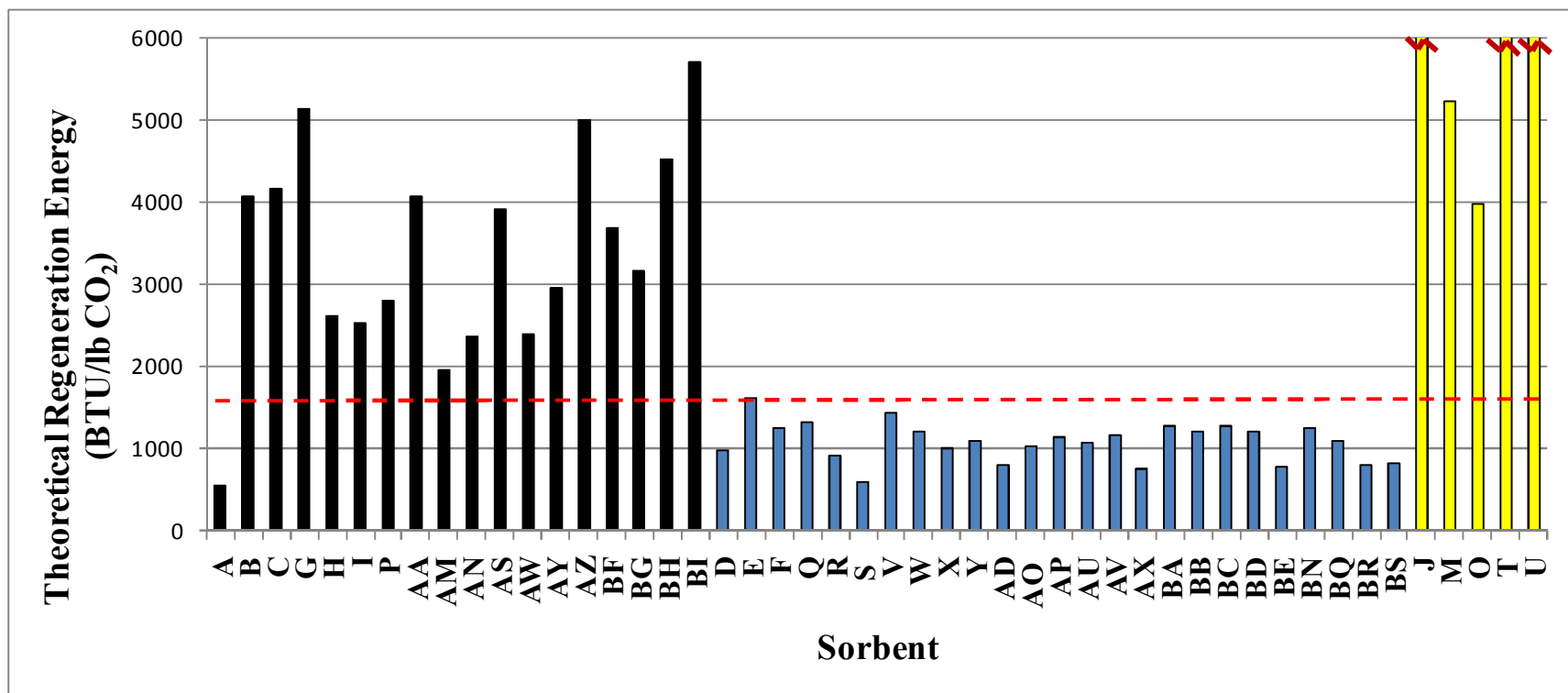
Figure 1: Summary of Laboratory-Scale Sorbent Screening Results

1 kW Pilot Slipstream: Equipment Description

Working with engineers at Southern Company, ADA-ES has designed and fabricated a unique 1 kW pilot-scale system designed specifically to test CO_2 sorbents. The system consists of three major components: a circulating fluidized bed reactor for adsorption (referred to as the riser), a heated fluidized bed for regeneration (regenerator), and a cooling section. The physical breakdown of the sorbent (i.e. attrition) in the 1kW pilot is minimized as much as possible by limiting the number of moving components. In the current design, the only moving part is a rotary valve located at the outlet of the sorbent cooler. This is used to control the sorbent circulation rate. In addition to the regeneration energy, the sorbent replacement cost represents a significant potential cost for full-scale operation with solid sorbents. Thus, minimizing process components that may contribute to attrition is important.

A sketch of the system with the main components labeled is provided in Figure 2. A 3D model sketch and photo of the 1 kW CO_2 capture system are provided in Figure 3. The system is designed for approximately 5 acfm of treated flue gas through the riser, where it entrains and reacts with the sorbent. This system was designed to be transportable and will be used at several power plants. The flue gas used at the first test site, Luminant's Martin Lake Steam Electric Station, was drawn from a duct downstream of a wet FGD system. Because supported amine sorbents are negatively affected by the presence of SO_2, most of the SO_2 was removed prior to the CO_2 capture system with an additional 1 kW scale scrubber.

The riser temperature was designed with jacketed cooling to maintain the temperature at typical scrubber outlet temperatures, or approximately 130°F (~55°C). Although the riser for the pilot system is only 1 inch in diameter, it is 40 feet tall, to allow evaluations of reaction time during 1kW pilot testing. A full-scale riser height above 40-feet was not considered reasonable. This height provides a contact time of approximately 3 seconds. There is also an added option for sorbent recirculation using an internal circulating fluidized bed (ICFB) located at the top of the riser if additional contact time is required. If the riser scale was increased so that it could treat a larger amount of gas flow, only the diameter of would be increased (i.e. the height would not change).

After the sorbent adsorbed the CO_2 in the riser and ICFB, it was transported to the regenerator. The regenerator consisted of a fluidized bed with external and internal electric heaters. The fluidization gas in the regenerator consisted of either dry N_2, humidified N_2 and/or CO_2. In a commercial system, N_2 will not be a viable option for the fluidization gas since sequestration requires a high purity stream of CO_2 and using N_2 as the fluidization gas dilutes the desorbed CO_2. When N_2 is used at the 1 kW scale it is used as a surrogate for steam, which would be a viable option for a fluidizing gas in a commercial system because it can be condensed from the regeneration gas stream. In the pilot system, the large wall surface area to sorbent volume significantly increases the risk and challenges associated with steam condensation in the regenerator. The regeneration exit gas, consisting mainly of CO_2 and moisture, could be further purified through condensation.
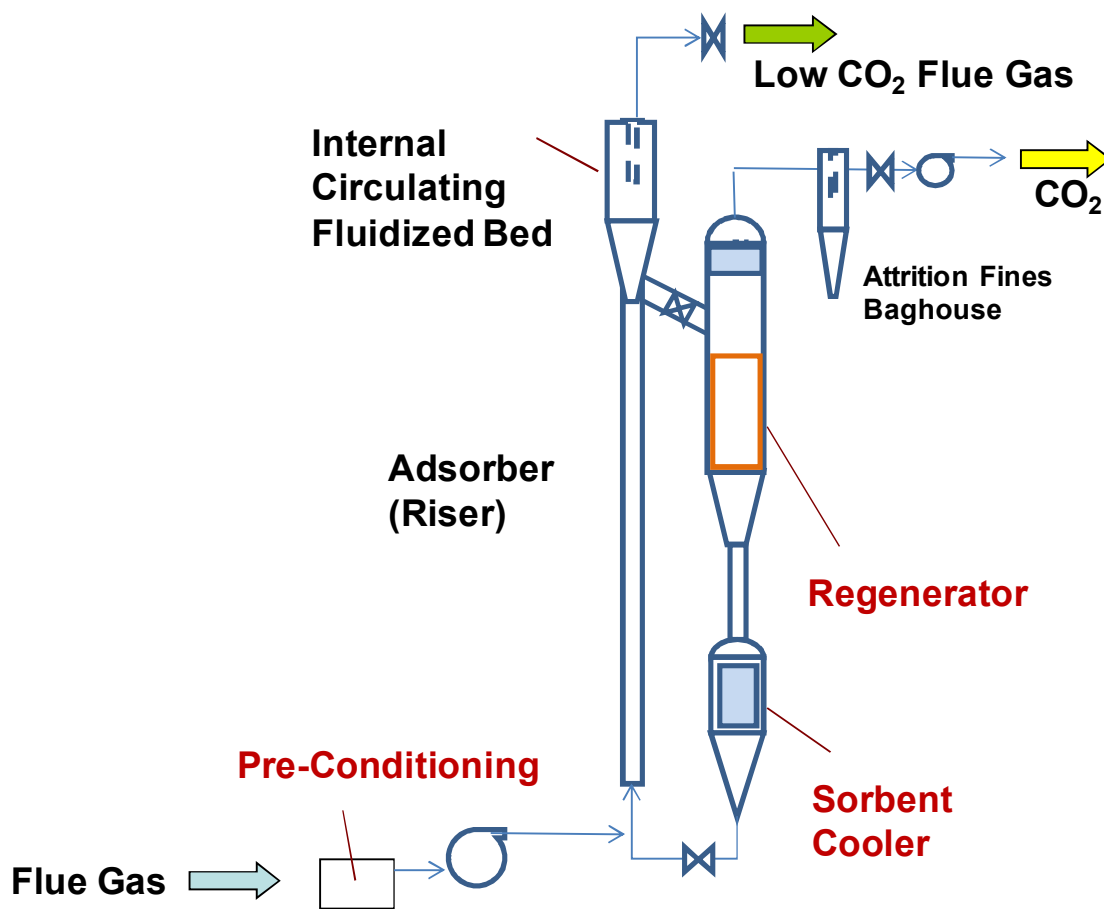
Figure 2: Sketch of 1 kW Pilot

During testing at Martin Lake, regeneration temperatures were in the range of 210°F to 250°F (100°C to 120°C). The maximum residence time in the regenerator was approximately 60 minutes, although this was in part a function of the current test scale. A small pump was used to extract the enriched CO_2 stream.

After the sorbent was heated in the regenerator and the CO_2 was removed, the sorbent was directed through a cooler that utilized jacketed cooling to reduce the temperature of the sorbent to approximately that of the riser. The circulation of the sorbent was controlled via a rotary valve downstream of the sorbent cooler. After the sorbent was cooled it was re-introduced to the riser, and the recirculation was continued. In a commercial system it will be important to find ways to minimize the energy burden on the power plant by integrating heat transfer between the different components of the CO_2 capture system as well as the CO_2 compressors, condensers, etc.

Figure 3: 3D Model Sketch and Photo of 1 kW System

Experimental Procedure

During characterization tests of Sorbent R, flue gas for the 1kW slipstream was extracted from downstream of an existing wet SO_2 scrubber at a plant firing a blend of lignite and PRB coals. The 1 kW pilot included an additional scrubber to maintain the SO_2 concentrations below 10 ppm. The temperature of the flue gas at the inlet to the riser was approximately 130°F and the CO_2 concentration was usually in the range of 13-14%.

The 1 kW pilot was operated continuously as well as in batch mode. Regardless of the operation mode, approximately 80 lbs of sorbent was loaded into the system. During continuous operation the sorbent was continuously circulated at a rate of 40 lb/hr. Flue gas entrained the sorbent and carried it through the riser while the majority of the CO_2 capture occurred. Fluidizing air was used to circulate sorbent in the ICFB, which promoted some additional adsorption. The set point temperatures for the electric heaters in the regenerator were selected in order to maintain the sorbent temperature at approximately 212°F. The sorbent was continuously circulated through the system while the CO_2 concentration at the riser inlet, ICFB outlet, and regenerator outlet were all monitored.

The system was designed to accommodate considerably longer regeneration times compared to adsorption times. However, with sorbent R the regeneration time required was significantly longer than the design could accommodate with continuous operation. Therefore, the system was operated in batch mode to provide adequate regeneration time. In batch mode, the adsorption was carried out in the same manner as during continuous operation. However, in

order to fully regenerate the sorbent, the entraining gas in the riser was switched to air to reduce the CO_2 concentration from nominally 13% to nominally 300 ppm. The sorbent was circulated at a rate of 20, 40, or 60 lb/hr until the CO_2 concentration in the regenerator exit gas was acceptable (in most cases <1%), indicating that the material had been passed through the regenerator enough times to release most of the captured CO_2.

RESULTS AND DISCUSSION

The first tests conducted using sorbent R were conducted in continuous operation mode. The CO_2 inlet, outlet, and removal levels for one test sequence are provided in Figure 4.
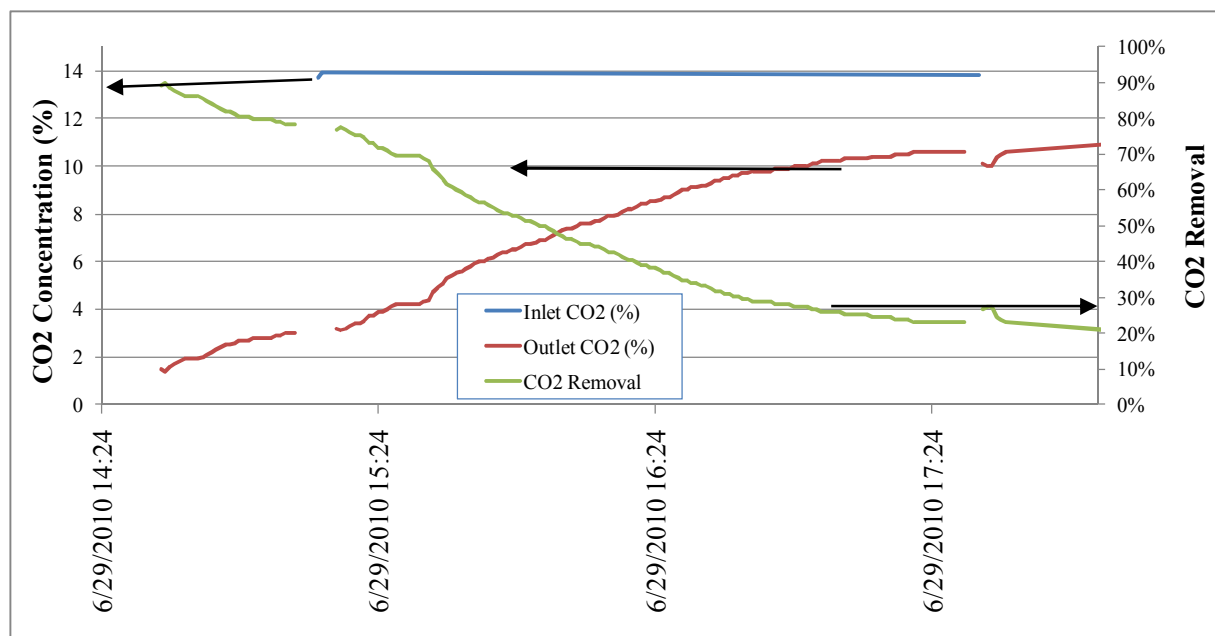
Figure 4: 1 kW Sorbent R Results during Continuous Operation

As has been observed previously when fresh sorbent was used, approximately 90% CO_2 capture was achieved at the lowest sorbent circulation rate identified in the test plan (40 lb/hr). During the test shown in the figure, the regenerator temperature was set below the temperature required for significant regeneration to determine when spent sorbent had passed through the system and began to re-enter the riser. However, even as the regenerator temperatures were increased, the CO_2 removal levels did not increase above 40%, indicating that full regeneration was not achieved during continuous operation with sorbent R. This can be attributed to the difference between the time required for sorbent R to regenerate in the fluidized bed regenerator and the time that the sorbent actually spent in the regenerator. The regeneration reaction was being slowed by the fact that sorbent R cannot be regenerated in high CO_2 concentration atmosphere. In the fluidized bed regenerator, the fluidizing gas is not constantly in contact with each sorbent particle to sweep away desorbed CO_2. Therefore, when utilizing this design, any sorbent that is unable to regenerate in pure CO_2 will take longer to regenerate than materials capable of some regeneration in pure CO_2. To ensure that the sorbent was capable of regenerating, the system was then operated in batch mode.

Ten adsorption/regeneration cycles were completed using the 1kW slipstream pilot operating in batch mode. The inlet, outlet, and regenerator CO_2 concentration as well as the CO_2 removal for one such cycle are provided in Figure 5. During this "typical" cycle, adsorption occurred from approximately 12:00 until 14:40 and regeneration began at 14:40 and continued past the 9-hr regeneration timeline shown on the figure. The difference in the time that the system was in adsorption mode versus regeneration mode can be attributed to the difference in reaction rates. The adsorption of CO_2 occurred rapidly; measuring the CO_2 concentration at different points in the riser revealed that a significant fraction of the adsorption occurs in the first 0.3 seconds. A faster regeneration reaction will lead to a smaller and simpler system.
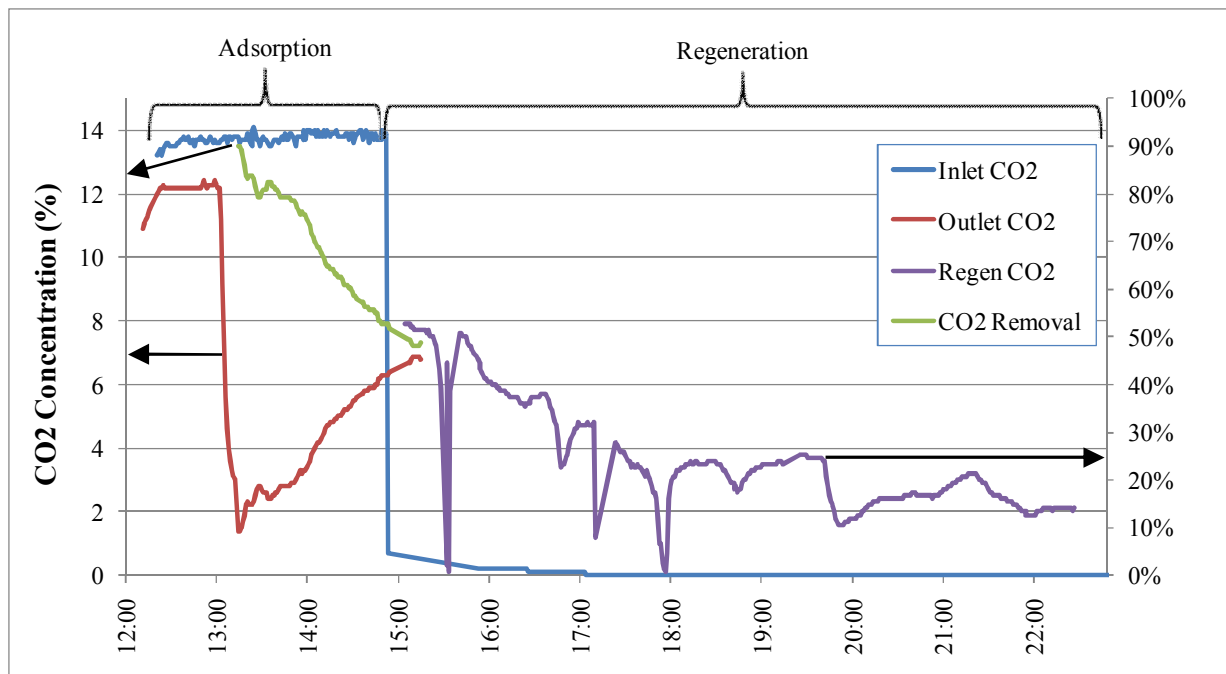
Figure 5: 1 kW Sorbent R Results in Batch Operation

The primary parameters varied between the ten batch mode adsorption cycles were 1) the CO_2 concentration at the regenerator exit when the regeneration step was concluded and 2) the sorbent circulation rate during regeneration. The circulation rate during adsorption was always 40 lb/hr and the temperature of the sorbent during regeneration was approximately 212°F. The maximum recorded CO_2 removal level is provided in Figure 6 for the ten cycles.
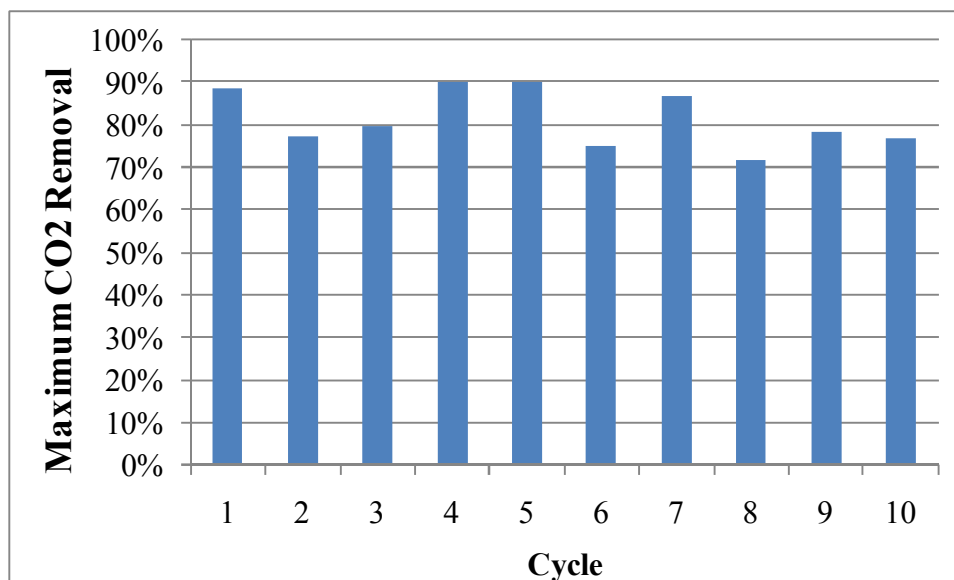
Figure 6: Maximum CO$_2$ Removal during Batch Operation

Based on the results from the batch operation tests, it was necessary to regenerate the sorbent until the regeneration gas contained <1% CO$_2$ to achieve 90% removal on the subsequent adsorption cycle. In addition, it was determined that lower sorbent circulation rates are preferable for regeneration. Greater CO$_2$ concentrations were measured in the regenerator exit gas when the sorbent circulation rate was 20 lb/hr versus those measured at 60 lb/hr. This could be attributed to better temperature control as well as longer residence time in the regenerator.

The 1 kW pilot equipment has been used to achieve 90% CO$_2$ removal using a supported amine sorbent. However, to realize continuous 90% CO$_2$ removal the two most important challenges that must be overcome are 1) to tightly control the temperatures in the riser as well as the regenerator and 2) develop a sorbent that can rapidly regenerate in high concentrations of CO$_2$.

SUMMARY

Retrofitting the existing fleet of coal-fired power plants for carbon capture and sequestration is one of the most important opportunities for a significant reduction in CO$_2$ emissions in the U.S. Among the many different post-combustions technologies being studied and developed, solid sorbents have emerged as one promising option. Testing solid sorbents at a meaningful scale using actual coal-fired flue gas is important for understanding the potential viability of solid sorbents for post-combustion CO$_2$ capture and to further development of the technology. This paper discussed results from 1 kW pilot testing of a supported amine sorbent. The sorbent/process combination was able to achieve 90% CO$_2$ capture during several adsorption/regeneration cycles. However, in order to achieve 90% CO$_2$ capture during continuous operation and produce a high purity CO$_2$ stream, the sorbent must be regenerable under a concentrated CO$_2$ atmosphere, the temperature of the system must be closely controlled, and the time sorbent must spend sufficient time in the regenerator. If these challenges can be overcome, there is great potential for a solid-sorbent based system to achieve 90% post-combustion CO$_2$ capture significantly while limiting operating costs by reducing the energy required for regeneration compared to other state of the art CO$_2$ capture systems.

ACKNOWLEDGEMENTS

DISCLAIMER

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KEY WORDS

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